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(71) Applicant(s)

Merck Patent GmbH

(Incorporated in the Federal Republic of Germany)

Frankfurter Strasse 250, D-6100 Darmstadt 1,
Federal Republic of Germany

(72) Inventor(s)

Mark John Goulding
Simon Greenfield
David Coates

(74) Agent and/or Address for Service

Venner Shipley & Co
368 City Road, London, EC1V 2QA, United Kingdom

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C623 C624 C634 C662 C666 C68Y C693 C694 C695
C697 C73Y C776 C80Y C821
C4X X12
U1S S1387 S2285

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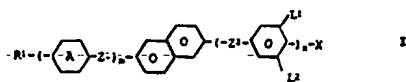
GB 2244710 A GB 2238309 A GB 2227019 A
US 4261651 A
Helv. Chim. Acta 68(5), 1406-26 Mol. Cryst. Liq. Cryst.,
Vol.99, 123-138 Bull. Soc. Chim. France 11-12, 2521-6

(58) Field of Search

UK CL (Edition L) C2C CHK CMB CNR CWR, C4X
INT CL⁵ C07C, C09K

(54) Liquid crystalline naphthalenes

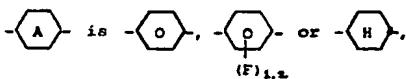
(57) Naphthalene derivatives of the formula I



in which

R¹ is an alkyl or alkenyl radical which is unsubstituted, monosubstituted by CN or CF₃ or at least monosubstituted by halogen and has 1 to 15 carbon atoms, it also being possible for one or more CH groups in these radicals to be replaced by -O-, -S-, -C(=O)-, -O-C(=O)- or -O-C(=O)-O-

in such a manner that oxygen atoms are not linked directly to one another,



m is 0, 1 or 2,

n is 0 or 1, where

m + n is 1 or 2,

Z¹ and Z² are each -CH₂CH₂-, -C≡C- or a single bond,

L¹ and L² are H or F,

X is an alkyl or alkoxy radical which is unsubstituted, monosubstituted by CN or CF₃ or at least monosubstituted by halogen and has 1 to 15 carbon atoms, or is OH, CN, NCS or Q-Y, where

Q is a single bond, (CF₂)_r or O(CF₂)_r

r is 1 or 2, and

Y is H, F, Cl or Br,

with the provisos that

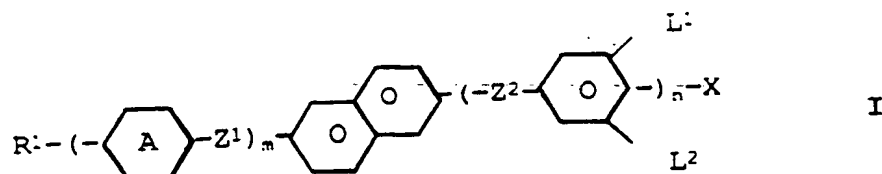
a) in the case where
m = 0, Z² = a single bond, n = 1 and X = CN or CF₃, L¹ is F,

b) in the case where
m = 0, Z² = a single bond, n = 1 and X = alkyl, alkoxy or F, L¹ and L² are identical and are F, can be used as components of liquid-crystalline media.


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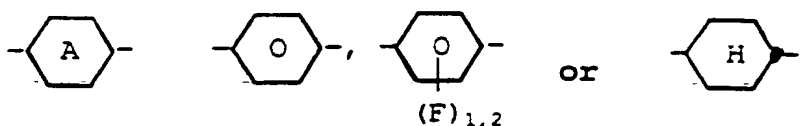
Naphthalene derivatives

5 The invention relates to naphthalene derivatives of the formula I



in which

10 R^1 is an alkyl or alkenyl radical which is unsubstituted, monosubstituted by CN or CF_3 , or at least monosubstituted by halogen and has 1 to 15 carbon atoms, it also being possible for one or more CH_2 groups in these radicals to be replaced, in each case independently of one another, by -O-, -S-, , -CO-, -CO-O-, -O-CO- or -O-CO-O- in such a manner that oxygen atoms are not linked directly to one another,



20 m is 0, 1 or 2,

n is 0 or 1, where

$m + n$ is 1 or 2,

Z^1 and Z^2 are each, independently of one another, $-CH_2CH_2-$, $-C=C-$ or a single bond,

25 L^1 and L^2 independently of one another, are H or F,

X an alkyl or alkoxy radical which is unsubstituted, monosubstituted by CN or CF₃ or at least monosubstituted by halogen and has 1 to 15 carbon atoms, or is OH, CN, NCS or Q-Y, where

Q is a single bond, (CF₂)_r or O(CF₂)_r,

r is 1 or 2, and

Y is H, F, Cl or Br,

with the provisos that

10 a) in the case where

m = 0, Z² = a single bond, n = 1 and X = CN or CF₃,
L¹ is F,

b) in the case where

15 m = 0, Z² = a single bond, n = 1 and X = alkyl, alkoxy or F, L¹ and L² are identical and are F.

20 The invention furthermore relates to the use of these compounds as components of liquid-crystalline media and to liquid-crystal and electro-optical display elements which contain the liquid-crystalline media according to the invention.

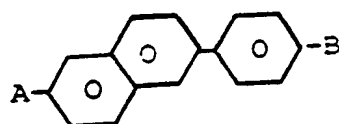
25 The compounds of the formula I can be used as components of liquid-crystalline media, in particular for displays based on the principle of the twisted cell, the guest-host effect, the effect of deformation of aligned phases or the effect of dynamic scattering.

The invention had the object of finding novel, stable, liquid-crystalline or mesogenic compounds which are suitable as components of liquid-crystalline media and in particular simultaneously have relatively low

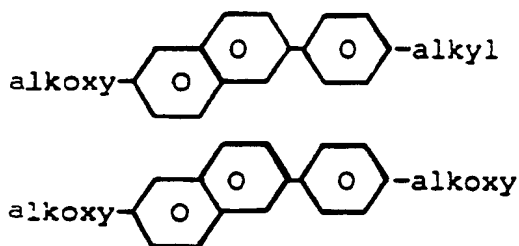
viscosity and relatively high dielectric and optical anisotropy.

It has now been found that compounds of the formula I are eminently suitable as components of liquid-crystalline media. In particular, they have relatively low viscosities. They can be used to obtain stable liquid-crystalline media having a broad mesophase range and advantageous values for the optical and dielectric anisotropy.

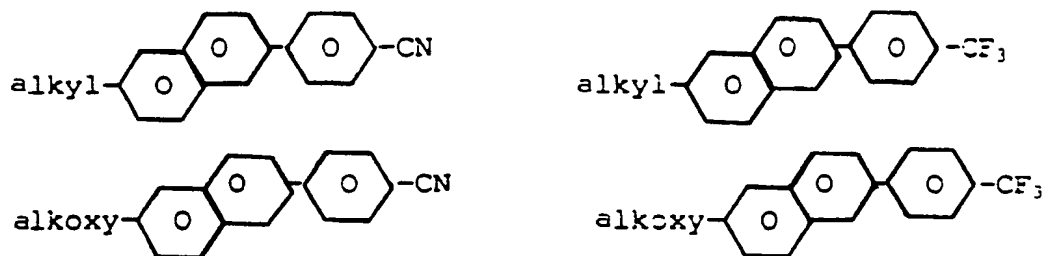
Liquid crystals of the formula



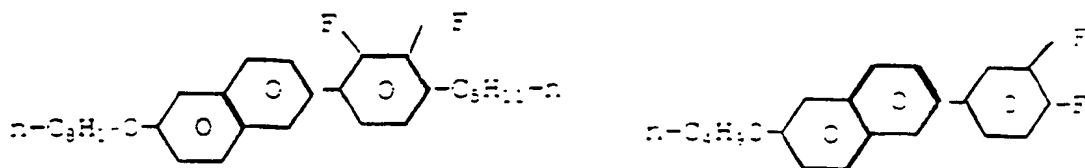
have already been disclosed. Bull. Soc. Chim. France (1975), 11-12 (2), 2521, describes compounds of the formulae



Helv. Chim. Acta 68 (5), 1406-26 (1985), discloses compounds of the following formulae



Finally, GB 2,227,019 mentions compounds of the formulae



However, in view of the very wide variety of areas of application of compounds of this type, it was desirable to have available further compounds which have properties precisely customised to the particular applications.

Compared with the phenylnaphthalene derivatives disclosed hitherto, the compounds according to the invention have a higher $\Delta\epsilon$ and particularly favourable elastic properties.

The compounds of the formula I have a broad range of applications. Depending on the choice of substituents, these compounds can be used as base materials from which liquid-crystalline media are predominantly composed; however, it is also possible to add compounds of the formula I to liquid-crystalline base materials from other classes of compound in order, for example, to modify the dielectric and/or optical anisotropy of a dielectric of this type and/or to optimise its threshold voltage and/or its viscosity.

Due to their particularly good stability, the compounds according to the invention are particularly suitable as components of TFT and projection display mixtures.

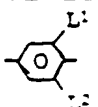
The compounds of the formula I are in particular suitable as components for liquid crystal media for displays which are based on the principle of polymer dispersed liquid crystals (pdlc) or polymer liquid crystals (pnlc) due to their favorable optical anisotropy and the dielectric anisotropy.

In the pure state, the compounds of the formula I are colourless and form liquid-crystalline mesophases in a temperature range which is favourably located for electro-optical use. They are stable chemically, thermically and to light.

The invention thus relates to the compounds of the formula I and to the use of these compounds as components of liquid-crystalline media. The invention furthermore relates to liquid-crystalline media containing at least one compound of the formula I and to liquid-

crystalline display elements, in particular electro-optical display elements, which contain media of this type.

For simplicity below, A denotes a radical of the

5 formula , and Nap denotes a naphthalene-2,6-diyl radical, Cyc denotes a 1,4-cyclohexylene radical and Phe denotes a 1,4-phenylene radical, it being possible for Cyc and/or Phe to be unsubstituted or monosubstituted or disubstituted by F or CN.

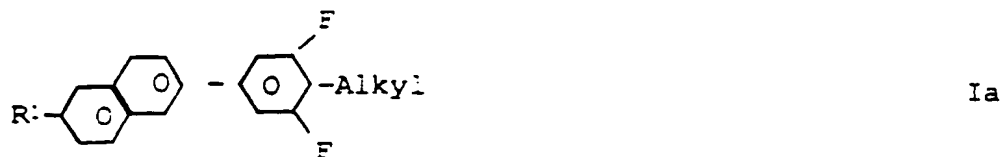
10 The compounds of the formula I include, in particular, compounds of the sub-formulae I1 to I57

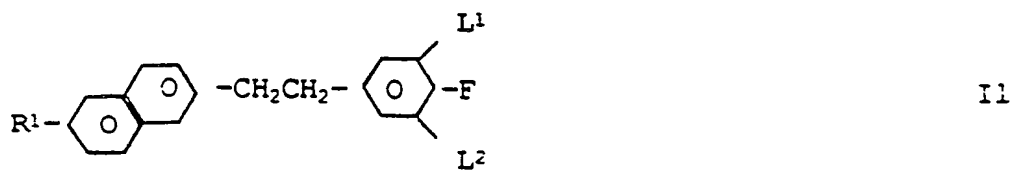
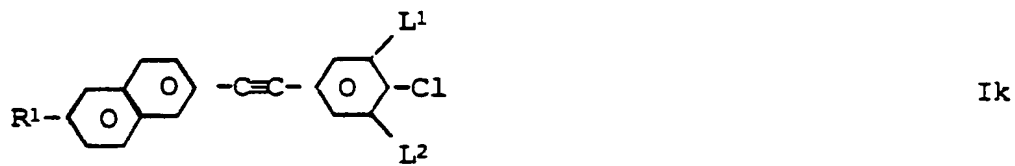
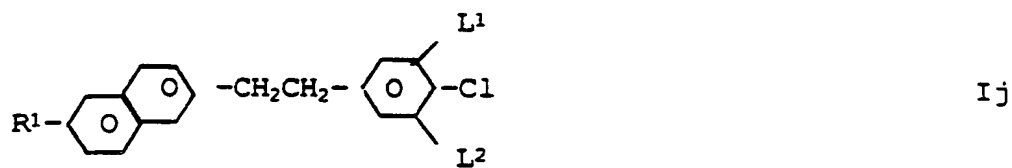
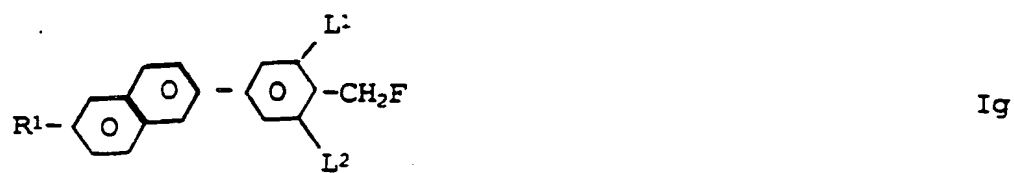
	R-Nap-A-X	I1
	R-Nap-Z ² -X	I2
	R-Cyc-Nap-A-X	I3
	R-Cyc-Nap-Z ² -X	I4
	R-Phe-Nap-A-X	I5
	R-Phe-Nap-Z ² -X	I6
	R-Cyc-Z ¹ -Nap-A-X	I7
	R-Cyc-Z ² -Nap-Z ² -X	I8
	R-Phe-Z ¹ -Nap-A-X	I9
	R-Phe-Z ² -Nap-Z ² -X	I10
	R-Cyc-Cyc-Nap-A-X	I11
	R-Cyc-Phe-Nap-A-X	I12
	R-Cyc-Z ¹ -Cyc-Nap-A-X	I13
15	R-Cyc-Z ¹ -Phe-Nap-A-X	I14
	R-Cyc-Cyc-Z ¹ -Nap-A-X	I15
	R-Cyc-Cyc-Z ¹ -Nap-Z ² -A-X	I16
	R-Cyc-Z ¹ -Cyc-Z ¹ -Nap-A-X	I17
	R-Cyc-Z ¹ -Cyc-Z ¹ -Nap-Z ² -A-X	I18
	R-Cyc-Phe-Z ¹ -Nap-A-X	I19
	R-Cyc-Z ¹ -Phe-Z ¹ -Nap-A-X	I20
	R-Cyc-Phe-Z ¹ -Nap-Z ² -A-X	I21
	R-Cyc-Z ¹ -Phe-Z ¹ -Nap-Z ² -A-X	I22
	R-Phe-Phe-Nap-A-X	I23

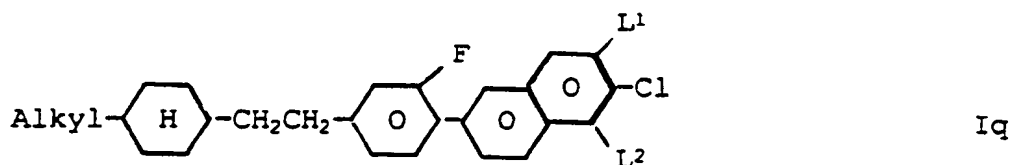
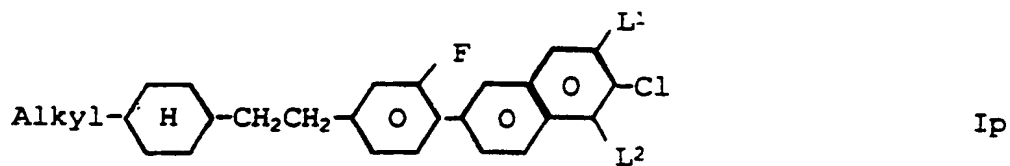
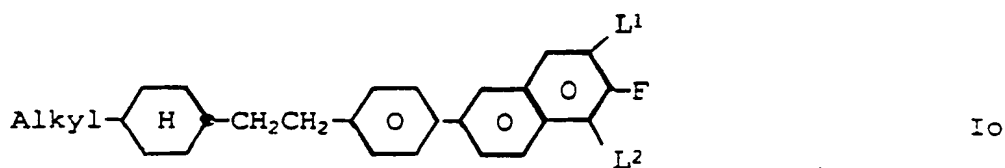
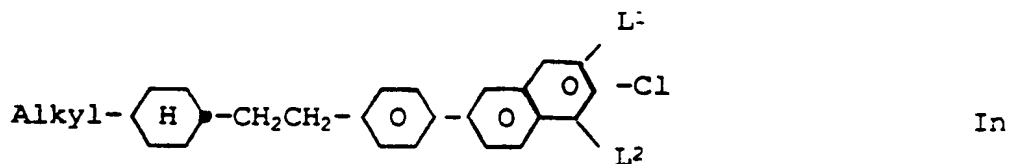
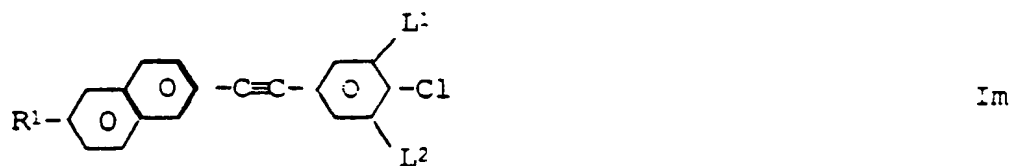
R-Phe-Z ¹ -Phe-Nap-A-X	I24
R-Phe-Z ¹ -Phe-Nap-Z ² -A-X	I25
R-Phe-Z ¹ -Phe-Nap-A-X	I26
R-Phe-Z ¹ -Phe-Z ¹ -Nap-A-X	I27
R-Phe-Z ¹ -Phe-Z ¹ -Nap-Z ² -A-X	I28
R-Phe-Phe-Z ¹ -Nap-A-X	I29
R-Phe-Phe-Z ¹ -Nap-Z ² -A-X	I30
R-Phe-Cyc-Nap-A-X	I31
R-Phe-Cyc-Nap-Z ² -A-X	I32
R-Phe-Z ¹ -Cyc-Nap-A-X	I33
R-Phe-Z ¹ -Cyc-Nap-Z ² -A-X	I34
R-Phe-Cyc-Z ¹ -Nap-A-X	I35
R-Phe-Cyc-Z ¹ -Nap-Z ² -A-X	I36
R-Phe-Z ¹ -Cyc-Z ¹ -Nap-A-X	I37
R-Phe-Z ¹ -Cyc-Z ¹ -Nap-Z ² -A-X	I38
R-Cyc-Nap-X	I39
R-Phe-Nap-X	I40
R-Cyc-Z ¹ -Nap-X	I41
R-Phe-Z ¹ -Nap-X	I42
R-Cyc-Cyc-Nap-X	I43
R-Cyc-Z ¹ -Cyc-Nap-X	I44
R-Cyc-Cyc-Z ¹ -Nap-X	I45
R-Phe-Cyc-Nap-X	I46
R-Phe-Z ¹ -Cyc-Nap-X	I47
R-Phe-Z ¹ -Cyc-Z ² -Nap-X	I48
R-Phe-Cyc-Z ¹ -Nap-X	I49
R-Phe-Phe-Nap-X	I50
R-Phe-Z ¹ -Phe-Nap-X	I51
R-Phe-Z ¹ -Phe-Z ¹ -Nap-X	I52
R-Phe-Phe-Z ¹ -Nap-X	I53

R-Cyc-Phe-Nap-X	I54
R-Cyc-Z ¹ -Phe-Nap-X	I55
R-Cyc-Z ¹ -Phe-Z ¹ -Nap-X	I56
R-Cyc-Phe-Z ¹ -Nap-X	I57

5 Some very particularly preferred smaller groups of compounds are those of the subformulae Ia to Iq (L = H or F):







X is preferably F, Cl, OCF₃, CF₃, OCH₂CF₃, CH₂F, CF₂H, OCH₂F, OCF₂H, CN, NCS, alkyl or alkoxy.

5 If R¹ is an alkyl radical and/or an alkoxy radical, this may be straight-chain or branched. It is preferably straight-chain, has 2, 3, 4, 5, 6 or 7 carbon atoms and accordingly is preferably ethyl, propyl, butyl, pentyl, hexyl, heptyl, ethoxy, propoxy, butoxy, pentoxy,

hexoxy or heptoxy, furthermore methyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, methoxy, octoxy, nonoxy, decoxy, undecoxy, dodecoxy, tridecoxy or tetradecoxy.

5 Oxaalkyl is preferably straight-chain 2-oxapropyl (= methoxymethyl), 2- (= ethoxymethyl) or 3-oxabutyl (= 2-methoxyethyl), 2-, 3- or 4-oxapentyl, 2-, 3-, 4- or 5-oxahexyl, 2-, 3-, 4-, 5- or 6-oxaheptyl, 2-, 3-, 4-, 5-, 6- or 7-oxaoctyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-oxanonyl, 10 or 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-oxadecyl.

 Compounds of the formula I containing branched wing groups R^1 may occasionally be of importance due to better solubility in the customary liquid-crystalline base materials, but in particular as chiral dopes if they 15 are optically active. Smectic compounds of this type are suitable as components of ferroelectric materials.

 Branched groups of this type generally contain not more than one chain branch. Preferred branched radicals R^1 are isopropyl, 2-butyl (= 1-methylpropyl), 20 isobutyl (= 2-methylpropyl), 2-methylbutyl, isopentyl (= 3-methylbutyl), 2-methylpentyl, 3-methylpentyl, 2-ethylhexyl, 2-propylpentyl, isopropoxy, 2-methylpropoxy, 2-methylbutoxy, 3-methylbutoxy, 2-methylpentoxy, 3-methylpentoxy, 2-ethylhexoxy, 1-methylhexoxy and 1-methylheptoxy. 25

 Compounds of the formula I which contain wing groups R^1 which are suitable for polycondensations are suitable for the preparation of liquid-crystalline polycondensates.

30 The formula I covers the racemates of these compounds and the optical antipodes, and mixtures thereof.

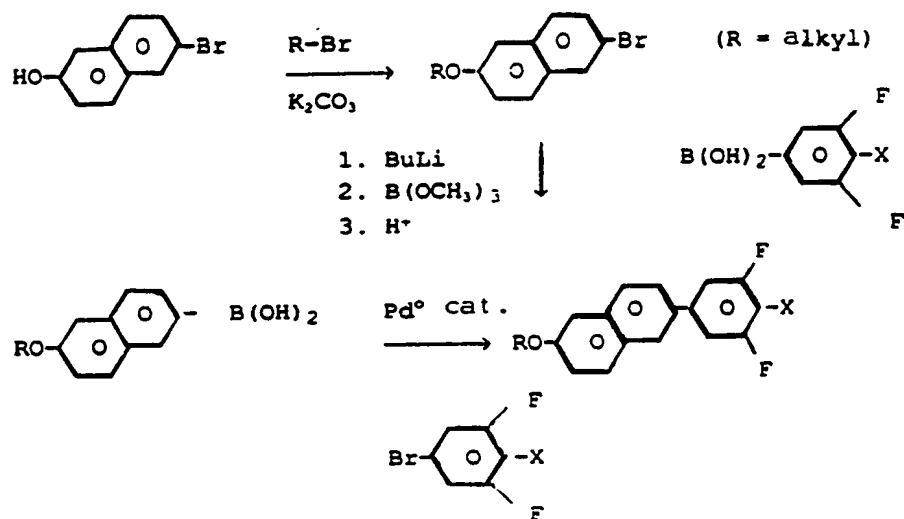
 Of these compounds of the formula I and of the sub-formulae, those are preferred in which at least one 35 of the radicals present therein has one of the preferred meanings indicated.

 The compounds of the formula I are prepared by methods known per se, as described in the literature (for

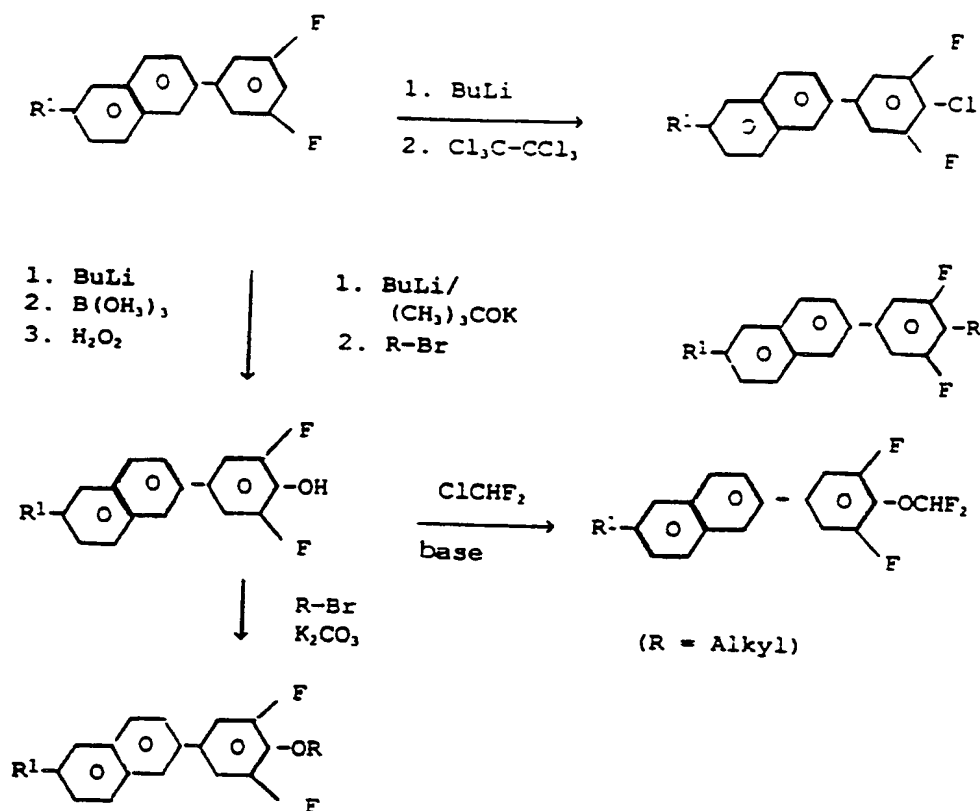
example in the standard works such as Houben-Weyl, Methoden der Organischen Chemie [Methods of Organic Chemistry], Georg-Thieme-Verlag), to be precise under reaction conditions which are known and suitable for said reactions. Use may also be made here of variants which are known per se, but are not described here in greater detail.

The compounds according to the invention can be prepared, for example, in accordance with the following schemes:

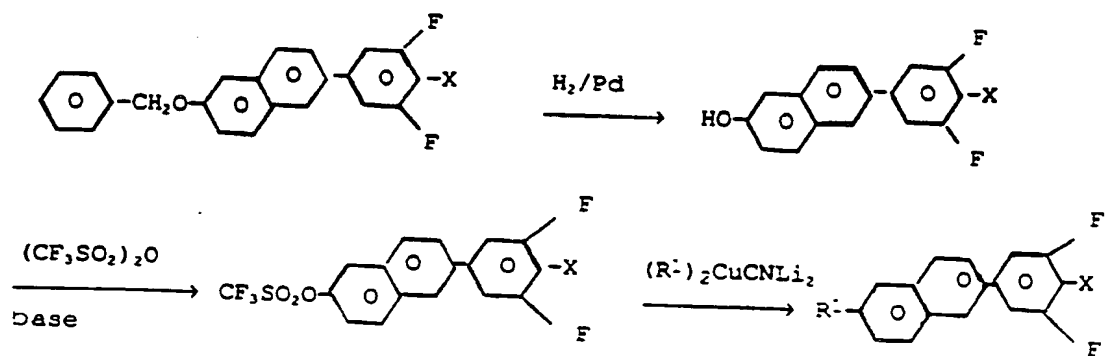
Scheme 1



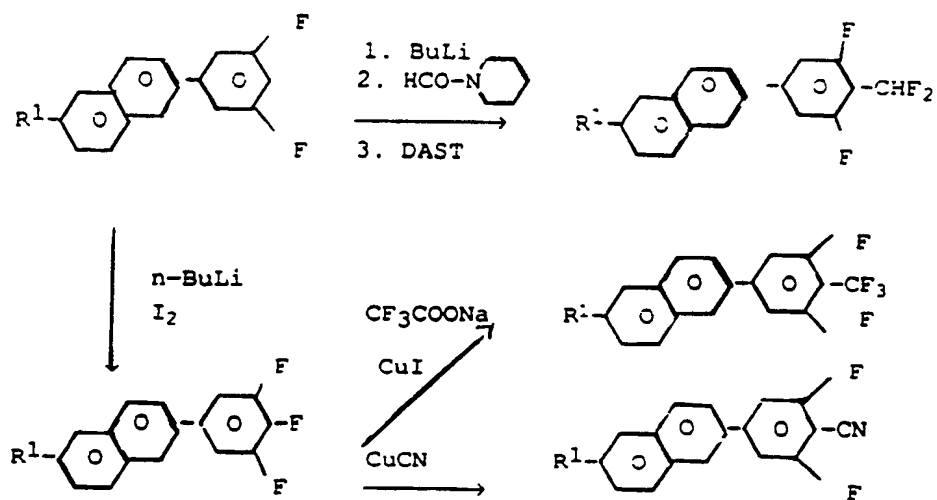
Scheme 2



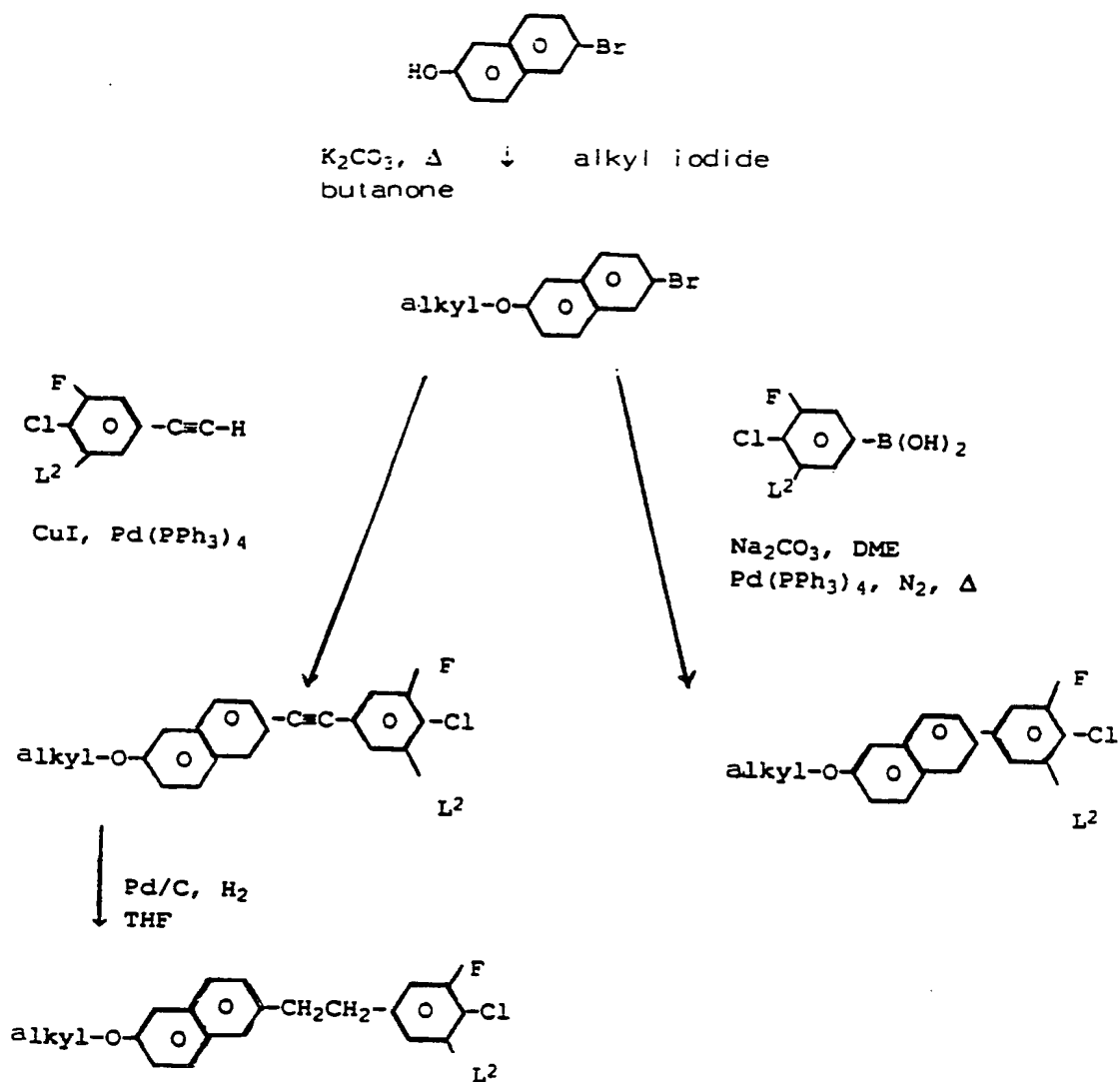
Scheme 3



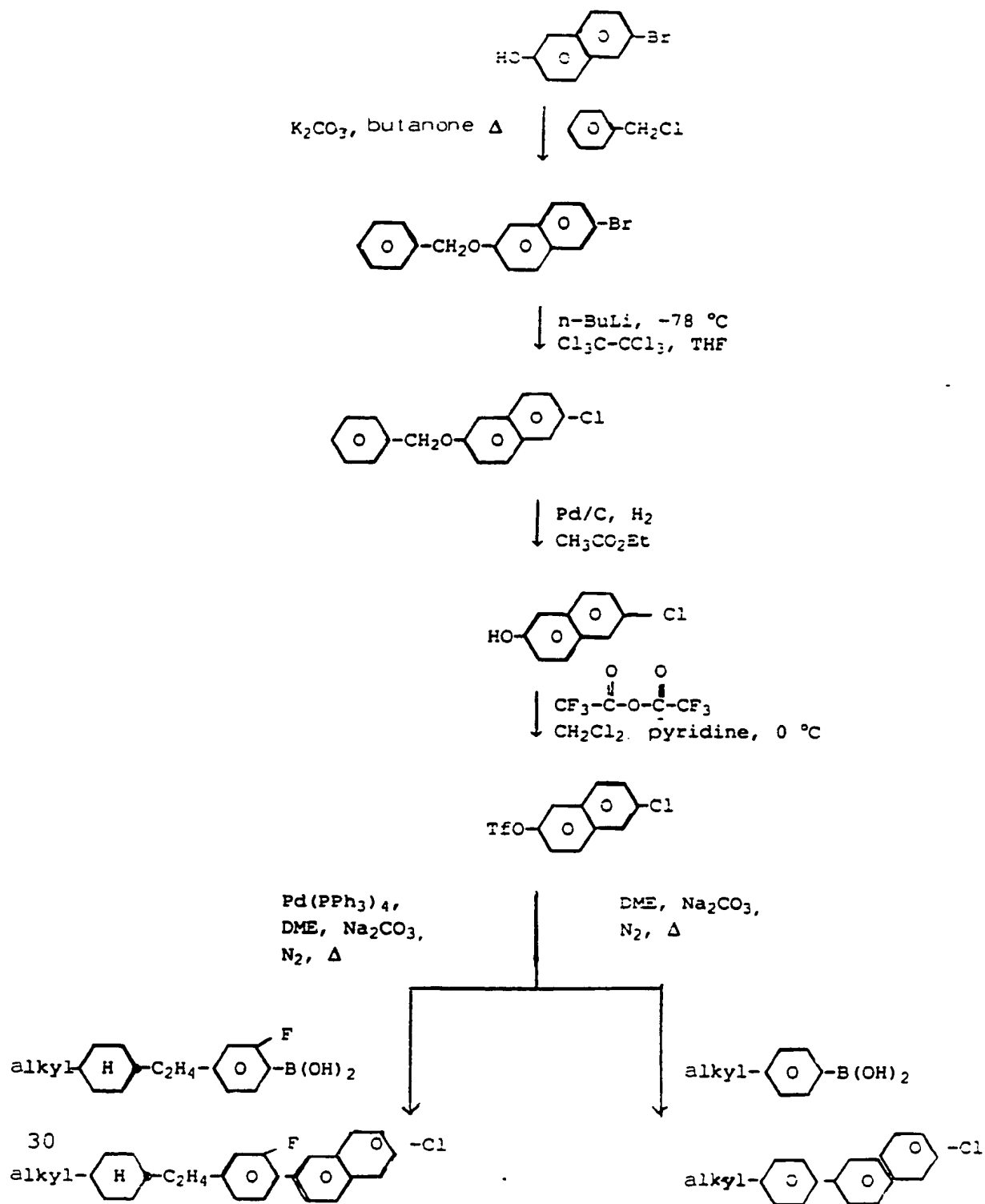
Scheme 4



Scheme 5



Scheme 6



Other methods of synthesis are obvious to a person skilled in the art.

The starting materials are known or can be prepared analogously to known compounds.

5 The liquid-crystalline media according to the invention preferably contain 2 to 40, in particular 4 to 30, components as further constituents besides one or more compounds according to the invention. These media very particularly preferably contain 7 to 25 components
10 besides one or more compounds according to the invention. These further constituents are preferably selected from nematic or nematogenic (monotropic or isotropic) substances, in particular substances from the classes of the azoxybenzenes, benzylideneanilines, biphenyls,
15 terphenyls, phenyl or cyclohexyl benzoates, phenyl or cyclohexyl esters of cyclohexanecarboxylic acid, phenyl or cyclohexyl esters of cyclohexylbenzoic acid, phenyl or cyclohexyl esters of cyclohexylcyclohexanecarboxylic acid, cyclohexylphenyl esters of benzoic acid, of cyclohexanecarboxylic acid and of cyclohexylcyclohexanecarboxylic acid, phenylcyclohexanes, cyclohexylbiphenyls,
20 phenylcyclohexylcyclohexanes, cyclohexylcyclohexanes, cyclohexylcyclohexenes, cyclohexylcyclohexylcyclohexenes, 1,4-bis-cyclohexylbenzenes, 4,4'-bis-cyclohexylbiphenyls, phenyl- or cyclohexylpyrimidines, phenyl- or cyclohexylpyridines, phenyl- or cyclohexyldioxanes, phenyl- or cyclohexyl-1,3-dithianes, 1,2-diphenylethanes, 1,2-dicyclohexylethanes, 1-phenyl-2-cyclohexylethanes, 1-cyclohexyl-2-(4-phenylcyclohexyl)ethanes, 1-cyclohexyl-2-biphenylethanes, 1-phenyl-2-cyclohexylphenylethanes,
30 optionally halogenated stilbenes, benzyl phenyl ethers, tolans and substituted cinnamic acids. The 1,4-phenylene groups in these compounds may also be fluorinated.

 The most important compounds suitable as further
35 constituents of media according to the invention can be characterized by the formulae 1, 2, 3, 4 and 5:

	R'-L-E-R"	1
	R'-L-COO-E-R"	2
	R'-L-OOC-E-R"	3
	R'-L-CH ₂ CH ₂ -E-R"	4
5	R'-L-C=C-E-R"	5

In the formulae 1, 2, 3, 4 and 5, L and E, which may be identical or different, are in each case, independently of one another, a bivalent radical from the group formed by -Phe-, -Cyc-, -Phe-Phe-, -Phe-Cyc-, -Cyc-Cyc-,
10 -Pyr-, -Dio-, -G-Phe- and -G-Cyc- and their mirror images, where Phe is unsubstituted or fluorine-substituted 1,4-phenylene, Cyc is trans-1,4-cyclohexylene or 1,4-cyclohexenylene, Pyr is pyrimidine-2,5-diyl or pyridine-2,5-diyl, Dio is 1,3-dioxane-2,5-diyl and G is
15 2-(trans-1,4-cyclohexyl)ethyl, pyrimidine-2,5-diyl, pyridine-2,5-diyl or 1,3-dioxane-2,5-diyl.

One of the radicals L and E is preferably Cyc, Phe or Pyr. E is preferably Cyc, Phe or Phe-Cyc. The media according to the invention preferably contain one
20 or more components selected from the compounds of the formulae 1, 2, 3, 4 and 5 in which L and E are selected from the group comprising Cyc, Phe and Pyr and simultaneously one or more components selected from the compounds of the formulae 1, 2, 3, 4 and 5 in which one
25 of the radicals L and E is selected from the group comprising Cyc, Phe and Pyr and the other radical is selected from the group comprising -Phe-Phe-, -Phe-Cyc-, -Cyc-Cyc-, -G-Phe- and -G-Cyc-, and optionally one or more components selected from the compounds of the
30 formulae 1, 2, 3, 4 and 5 in which the radicals L and E are selected from the group comprising -Phe-Cyc-, -Cyc-Cyc-, -G-Phe- and -G-Cyc-.

In the compounds of the sub-formulae 1a, 2a, 3a, 4a and 5a, R' and R" are in each case, independently of
35 one another, alkyl, alkenyl, alkoxy, alkenyloxy or alkanoyloxy having up to 8 carbon atoms. In most of these compounds, R' and R" are different from one another, one

of these radicals usually being alkyl or alkenyl. In the compounds of the sub-formulae 1b, 2b, 3b, 4b and 5b, R" is -CN, -CF₃, F, Cl or -NCS; in this case, R has the meaning given for the compounds of the sub-formulae 1a to 5a and is preferably alkyl or alkenyl. However, other variants of the proposed substituents in the compounds of the formulae 1, 2, 3, 4 and 5 are common. Many such substances or alternatively mixtures thereof are commercially available. All these substances can be obtained by methods which are known from the literature or analogously thereto.

Besides components from the group comprising the compounds 1a, 2a, 3a, 4a and 5a (Group 1), the media according to the invention preferably also contain components from the group comprising the compounds 1b, 2b, 3b, 4b and 5b (Group 2), whose proportions are preferably as follows:

Group 1: 20 to 90%, in particular 30 to 90%,
Group 2: 10 to 80%, in particular 10 to 50%,
the sum of the proportions of the compounds according to the invention and of the compounds from Groups 1 and 2 adding up to 100%.

The media according to the invention preferably contain 1 to 40%, in particular preferably 5 to 30%, of compounds according to the invention. Further preferred media are those which contain more than 40%, in particular 45 to 90%, of compounds according to the invention. The media preferably contain three, four or five compounds according to the invention.

The media according to the invention are prepared in a manner which is customary per se. In general, the components are dissolved in one another, expediently at elevated temperature. By means of suitable additives, the liquid-crystalline phases can be modified in accordance with the invention in a manner such that they can be used in all types of liquid-crystal display elements which have hitherto been disclosed. Additives of this type are known to those skilled in the art and are described in

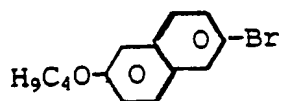
detail in the literatur (H. Kelker/R. Hatz, Handbook of
Liquid Crystals, Verlag Chemie, Weinheim, 1980). For
example, pleochroic dyes can be added for the production
of coloured guest-host systems, or substances can be
5 added to modify the dielectric anisotropy, the viscosity
and/or the orientation of the nematic phases.

The examples below are intended to illustrate the
invention without representing a limitation. Above and
below, percentages are percent by weight; all tempera-
10 tures are indicated in degrees Celsius. M.p. is melting
point, c.p. = clearing point. Furthermore, C = crystal-
line state, N = nematic phase, S = smectic phase and I =
isotropic phase. The numbers between these symbols
indicate the transition temperatures. Δn denotes optical
15 anisotropy (589 nm, 20°C), and the viscosity (mm²/sec) was
determined at 20°C.

"Customary work-up" means that water is added if
necessary, the mixture is extracted with methylene
chloride, diethyl ether or toluene, the organic phase is
20 separated off, dried and evaporated, the product is
purified by distillation under reduced pressure or
crystallisation and/or chromatography. The following
abbreviations are used:

BuLi	butyllithium
25 DMS	dimethyl sulphate
THF	tetrahydrofuran
TTPP	tetrakis(triphenylphosphine)palladium(0)

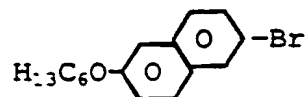
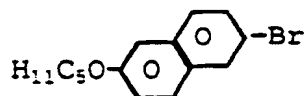
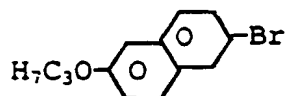
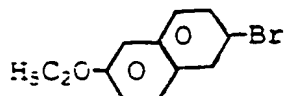
Example 1



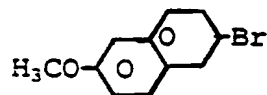
0.2 mol of 1-bromobutane in 100 ml of acetone are
30 added dropwise to a refluxing mixture of 0.2 mol of 2-
hydroxy-6-bromonaphthalene and 0.4 mol of potassium
carbonate dissolved in 500 ml of acetone. The mixture is
subsequently refluxed for 24 hours. The potassium

carbonate is filtered off, and the mixture is subsequently subjected to customary work-up.

The following compounds are prepared analogously:

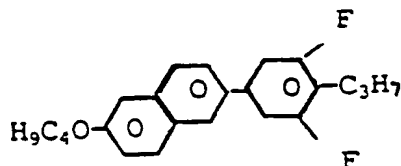


Example 2



- 5 0.25 mol of DMS is added in portions to a stirred solution of 0.2 mol of 2-hydroxy-6-bromonaphthalene and 0.25 mol of potassium hydroxide in water. The mixture is stirred for one hour at 70°C and subsequently overnight at room temperature. The mixture is then filtered, the
- 10 filtrate is washed with 10% sodium hydroxide solution, and the mixture is subjected to customary work-up.

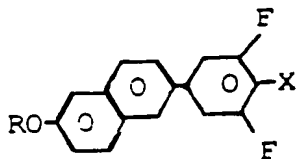
Example 3



- 15 10 mmol of 2-butoxy-6-bromonaphthalene in 30 ml of ethanol are added dropwise under a nitrogen atmosphere to 14 mmol of 1-propyl-2,6-difluorophenylboric acid (prepared from 4-propyl-3,5-difluorobromobenzene using magnesium and trimethyl borate), 60 ml of 2 M potassium carbonate solution and 0.5 mmol of TPP in 60 ml of

benzene. The mixture is refluxed for 24 hours and subsequently subjected to customary work-up.

The following novel compounds of the formula

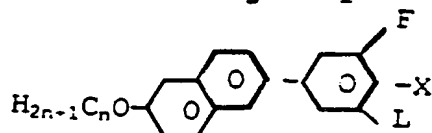


are obtained analogously from the corresponding precursors.

R	X
CH ₃	n-C ₂ H ₅
CH ₃	n-C ₃ H ₇
n-C ₂ H ₅	CH ₃
n-C ₂ H ₅	n-C ₂ H ₅
n-C ₂ H ₅	n-C ₃ H ₇
n-C ₂ H ₅	n-C ₄ H ₉
n-C ₂ H ₅	n-C ₅ H ₁₁
n-C ₃ H ₇	CH ₃
n-C ₃ H ₇	n-C ₂ H ₅
n-C ₃ H ₇	n-C ₃ H ₇
n-C ₃ H ₇	n-C ₄ H ₉
n-C ₄ H ₉	n-C ₅ H ₁₁
n-C ₄ H ₉	CH ₃
n-C ₄ H ₉	n-C ₂ H ₅
n-C ₄ H ₉	n-C ₄ H ₉
n-C ₄ H ₉	n-C ₅ H ₁₁

COc1ccc2cc3cc(F)c(F)c(F)c3cc2c1

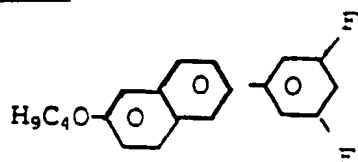
15 The following compounds of the formula



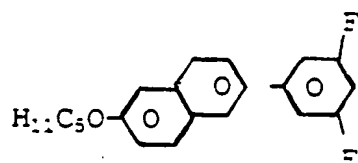
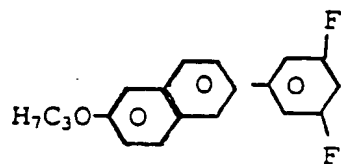
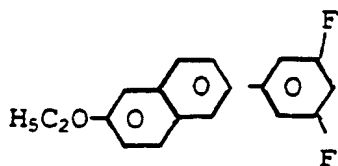
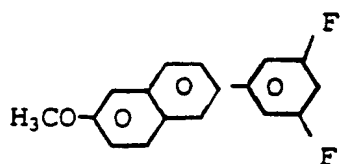
n	X	L
1	F	F
1	Cl	F
1	Cl	H
2	F	F
2	Cl	F
2	Cl	H
3	F	F
3	Cl	F
3	Cl	H
3	CN	F

n	X	L
4	Cl	F
4	Cl	H
5	F	F
5	Cl	F
5	Cl	H
5	CN	F

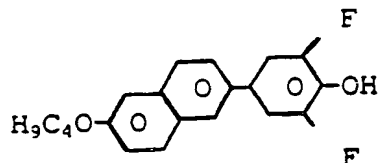
Example 5



7.0 mmol of 3,5-difluorophenylboric acid are reacted with 5.2 mmol of 2-butoxy-6-bromonaphthalene analogously to Example 2. The following compounds are
5 obtained analogously from the corresponding precursors:

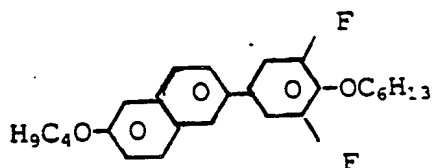


Example 6



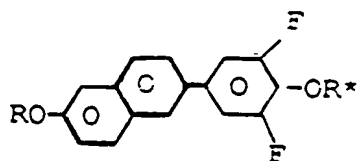
26 mmol of n-BuLi are added dropwise at -70°C to a mixture comprising 26 mmol of 3,5-difluorophenyl-6-butoxynaphthalene from Example 5 and 60 ml of THF. After the mixture has been stirred at -70°C for one hour, 36 mmol of trimethyl borate are added dropwise at the same temperature. The mixture is stirred for a further 0.5 hour, and 42 mmol of acetic acid are then added dropwise at -20°C. The mixture is subsequently warmed to 30°C, 4.2 mmol of H₂O₂ are added dropwise at this temperature, and the mixture is stirred for two hours at from 50 to 60 °C. The mixture is cooled to room temperature, and a 5% sodium dithionite solution is added. Phase separation and customary work-up give the difluorophenol derivative.

Example 7



The product obtained in Example 6 is reacted with hexyl iodide in acetone under reflux in the presence of potassium carbonate to give the hexyl ether. Customary work-up and chromatography on silica gel using hexane give the ether in pure form.

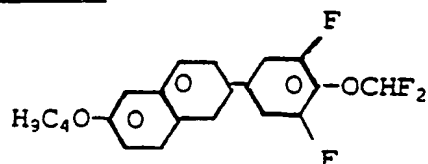
The following compounds of the formula



are obtained analogously from the corresponding precursors.

R	R*
CH ₃	CH ₃
CH ₃	C ₂ H ₅
CH ₃	C ₃ H ₇
n-C ₂ H ₅	CH ₃
n-C ₂ H ₅	C ₂ H ₅
n-C ₂ H ₅	n-C ₃ H ₇
n-C ₂ H ₅	n-C ₄ H ₉
n-C ₂ H ₅	n-C ₅ H ₁₁
n-C ₃ H ₇	CH ₃
n-C ₂ H ₅	C ₂ H ₅
n-C ₂ H ₅	n-C ₃ H ₇
n-C ₂ H ₅	n-C ₄ H ₉
n-C ₂ H ₅	n-C ₅ H ₁₁
n-C ₂ H ₅	n-C ₆ H ₁₃
n-C ₄ H ₉	CH ₃
n-C ₄ H ₉	C ₂ H ₅
n-C ₄ H ₉	n-C ₃ H ₇
n-C ₄ H ₉	n-C ₄ H ₉
n-C ₄ H ₉	n-C ₅ H ₁₁
n-C ₅ H ₁₁	C ₂ H ₅
n-C ₅ H ₁₁	n-C ₃ H ₇
n-C ₅ H ₁₁	n-C ₄ H ₉
n-C ₅ H ₁₁	n-C ₅ H ₁₁
n-C ₅ H ₁₁	n-C ₆ H ₁₃

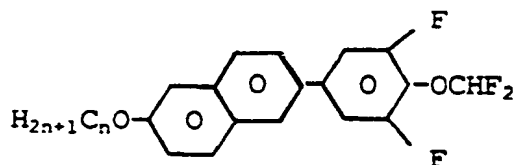
Example 8



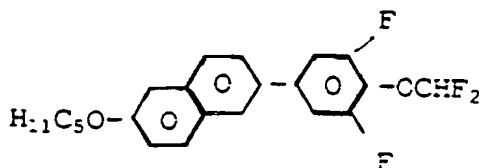
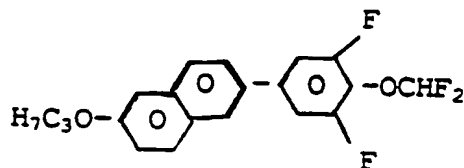
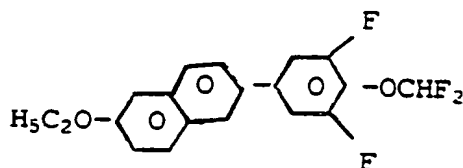
3.1 g of a 32% sodium hydroxide solution and 0.5 g of tetrabutylammonium hydrogen sulphate are added to 0.01 mol of the difluorophenol derivative from Example 6 in THF, and the mixture is warmed to 50°C. Chlorodi-
 5 fluoromethane is added to the stirred mixture until it condenses on a condenser cooled by means of dry ice. After cooling, the THF solution is filtered. The mixture is subsequently subjected to customary work-up.

10

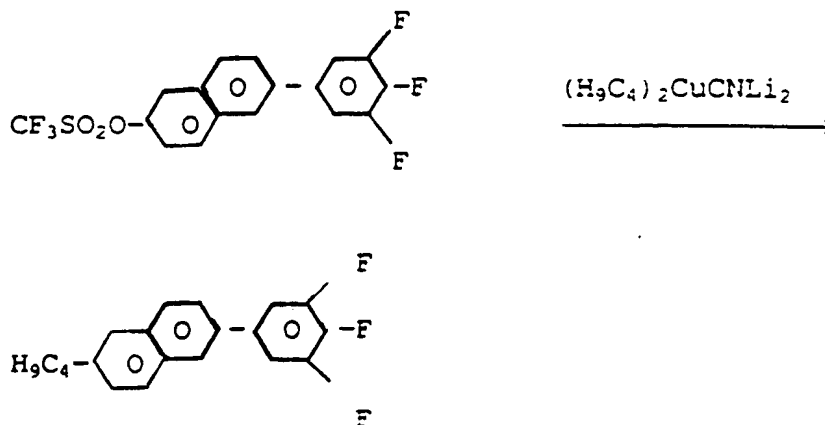
The following compounds of the formula



are prepared analogously from the corresponding precursors:

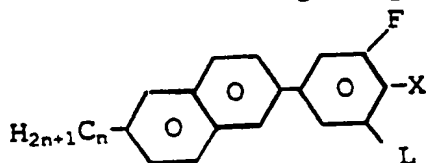


Example 9



0.1 mol of BuLi (in the form of a 15% solution in n-hexane) is added dropwise at -70°C to a suspension of 0.05 mol of CuCN in 100 ml of THF, and the mixture is then allowed briefly to warm to -20°C . A solution of 0.02 mol of the triflate in THF is then added dropwise at -70°C , and the mixture is then allowed to warm to -20°C and is subsequently stirred at this temperature for 6 hours, hydrolysed and subjected to customary work-up.

The following compounds of the formula



are prepared analogously from the corresponding starting compounds:

n	X	L
2	CH ₃	F
2	C ₂ H ₅	F
2	n-C ₃ H ₇	F
2	n-C ₄ H ₉	F
2	n-C ₅ H ₉	F
2	OC ₂ H ₅	F
2	OC ₃ H ₇	F

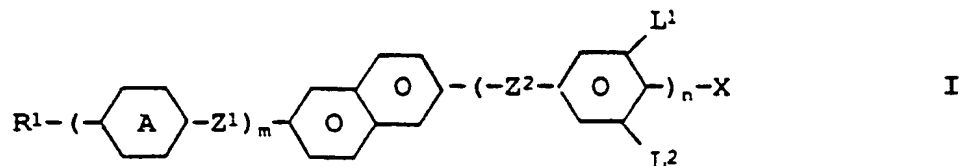
n	X	L
2	OC ₄ H ₉	F
2	F	F
2	Cl	H
2	Cl	F
2	CN	F
2	OH	H
2	OH	F
2	OCF ₃	F
2	OCHF ₂	F
2	OCH ₂ F	H
2	CF ₃	F
2	CHF ₂	F
3	F	F
3	Cl	H
3	Cl	F
3	OH	H
3	OH	F
3	CN	F
3	CF ₃	F
3	OCF ₃	F
3	CHF ₂	F
3	CH ₂ F	F
3	OCHF ₂	F
3	OCH ₂ F	F
4	Cl	H
4	Cl	F
4	OH	H
4	OH	F
4	CN	F
4	CF ₃	F
4	CCF ₃	F

n	X	L
4	CHF_2	F
4	CH_2F	F
4	OCHF_2	F
4	OCH_2F	F
5	F	F
5	Cl	H
5	Cl	H

Merck Patent Gesellschaft
mit beschränkter Haftung
6100 Darmstadt

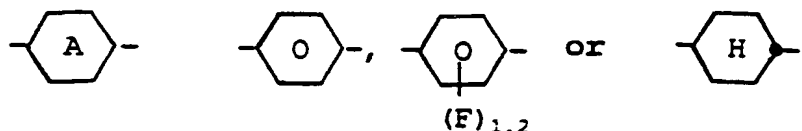
Patent claims

- 5 1. Naphthalene derivatives of the formula I



in which

10 R^1 is an alkyl or alkenyl radical which is unsubstituted, monosubstituted by CN or CF_3 , or at least monosubstituted by halogen and has 1 to 15 carbon atoms, it also being possible for one or more CH_2 groups in these radicals to be replaced, in each case independently of one another, by $-O-$, $-S-$, $-\text{C}_4\text{H}_6-$, $-CO-$, $-CO-$
15 $O-$, $-O-CO-$ or $-O-CO-O-$ in such a manner that oxygen atoms are not linked directly to one another,



m is 0, 1 or 2,

20 n is 0 or 1, where

$m + n$ is 1 or 2,

Z^1 and Z^2 are each, independently of one another, $-CH_2CH_2-$, $-C=C-$ or a single bond,

L^1 and L^2 independently of one another, are H or F,

X is an alkyl or alkoxy radical which is unsubstituted, monosubstituted by CN or CF₃, or at least monosubstituted by halogen and has 1 to 15 carbon atoms, or is OH, CN, NCS or Q-Y, where

Q is a single bond, (CF₂)_r or O(CF₂)_r,

r is 1 or 2, and

Y is H, F, Cl or Br,

with the provisos that

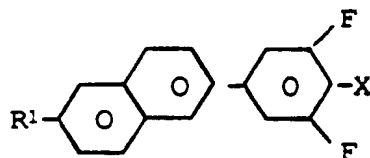
a) in the case where

m = 0, z² = a single bond, n = 1 and X = CN or CF₃, L¹ is F,

b) in the case where

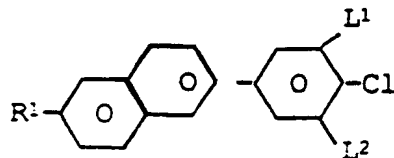
m = 0, z² = a single bond, n = 1 and X = alkyl, alkoxy or F, L¹ and L² are identical and are F.

2. Compounds of the formula



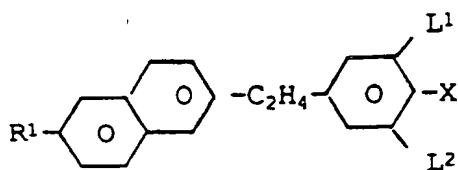
in which R¹ is as defined in Claim 1, and X is F, Br, CF₃, CHF₂, CH₂F, OCF₃, OCH₂F, OCHF₂ or CF₂Cl.

3. Compounds of the formula



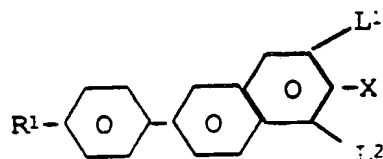
in which R¹, L¹ and L² are as defined in Claim 1.

4. Compounds of the formula



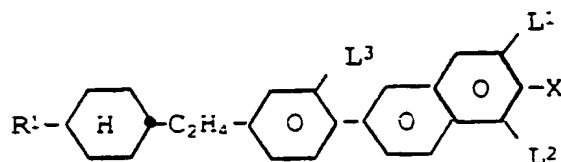
in which R^1 , X , L^1 and L^2 are as defined in Claim 1.

5. Compounds of the formula



in which R^1 , X , L^1 and L^2 are as defined in Claim 1.

6. Compounds of the formula



5 in which R^1 , X , L^1 and L^2 are as defined in Claim 1 and L^3 is H or F.

7. Use of the compounds of the formula I as components of liquid-crystalline media.

8. Liquid-crystalline medium containing at least two
10 liquid-crystalline components, characterised in that it contains at least one compound of the formula I.

9. Liquid-crystal display element, characterised in that it contains a liquid-crystalline medium according to Claim 8.

Relevant Technical Fields

- (i) UK Cl (Ed.L) C2C CHK CMB CNR CWR; C4X
(ii) Int Cl (Ed.5) C07C C09K

Search Examiner
P N DAVEY

Date of completion of Search
2 NOVEMBER 1993

Databases (see below)

- (i) UK Patent Office collections of GB, EP, WO and US patent specifications.

Documents considered relevant
following a search in respect of
Claims :-
1-9

(ii)

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- X:** Document indicating lack of novelty or of inventive step. **P:** Document published on or after the declared priority date but before the filing date of the present application.
Y: Document indicating lack of inventive step if combined with one or more other documents of the same category. **E:** Patent document published on or after, but with priority date earlier than, the filing date of the present application.
A: Document indicating technological background and/or state of the art. **&:** Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages	Relevant to claim(s)
X	GB 2244710 A (SEC STATE DEFENCE) see eg formula I	1, 7-9 at least
X	GB 2238309 A (SEC STATE DEFENCE) see eg formula I	1, 7-9 at least
X	GB 2227019 A (SEC STATE DEFENCE) see eg formula I	1, 7-9 at least
X	US 4261651 (SEC STATE DEFENCE) see esp ex 7	1, 4, 7-9 at least
X	Helv. Chim. Acta 68(5), 1406-26	1, 7-9 at least
X	Mol. Cryst. Liq. Cryst., Vol 99, 123-138	1, 7-9 at least
X	Bull. Soc. Chim. France 11-12, 2521-6	1 at least

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